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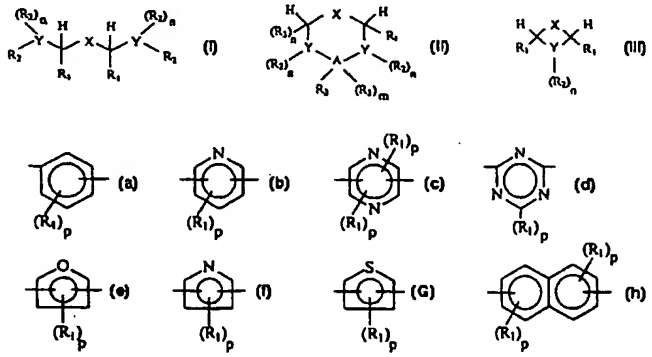
(54) Title: STABILIZATION OF POLYMERS AFTER EXPOSURE TO OXIDATION



(57) Abstract

Disclosed is polyvinyl chloride, polyvinylidene chloride, polycarbonate, polyethylene, polypropylene, polyamide, polyimide, polyether, polyester, or polyvinyl acetate containing about 0.005 to about 10 phr of a stabilizer having general formula (I), (II) or (III): where A is C, P, Sn, Si, or B, X is =C=C=, -C ≡ C-, (a), (b), (c), (d) each Y is idependently selected from O, S, and N, each R is idependently selected from hydrogen, alkyl from C_1 to C_{24}, aryl from C_6 to C_{24}, alkaryl from C_7 to C_{24} and aralkyl from C_7 to C_{24}, each R_1 is independently selected from R, OR, RCO, ROCO, $ROCO_2$, $P(R)_2$, $P(OR)_2$, $PR(OR)$, $N(R)_2$, $(R)_2NCO$, $(R)_2NCO_2$, SR, and halogen, where two R_1 groups can be bridged together to form a ring, each R_2 is independently selected from R, RCO, ROCO, $P(OR)_2$, $Sn(R)_q(OR)_{3-q}$, $SnR_q(OCOR)_{3-q}$, $Si(R)_q(OR)_{3-q}$, and $BR_q(OR)_{2-q}$, where two R_2 groups can be bridged together to form a ring, each R_3 is independently selected from R, RCO, ROCO, $ROCO_2$, OR, SR, $N(R)_2$, $OP(R)_2$, and $OP(OR)_2$, m is 0 when A is P or B and is 1 when A is Sn, SI, or C, n is 0 when Y is O or S and is 1 when Y is N, p is 0 to 4, depending on the number of available sites, and q is 0 to 3 for the tin stabilizers and 0 to 2 for the boron stabilizers. Also disclosed is a method of preventing these polymers from discoloring after exposure to oxidation.

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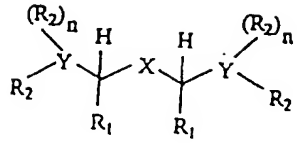
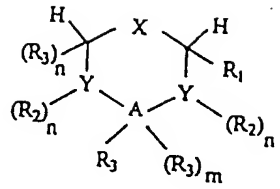
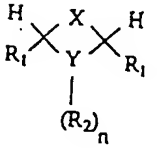
"STABILIZATION OF POLYMERS AFTER EXPOSURE TO OXIDATION"

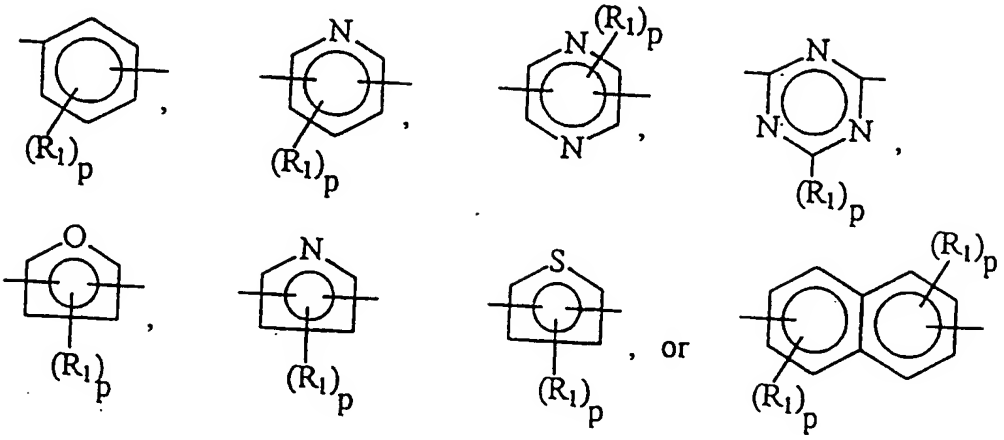
THIS INVENTION relates to the use of stabilizers to reduce the discoloration of certain polymers after they have been exposed to oxidation.

A number of different polymers, including polyvinyl chloride (PVC), polycarbonates, polyurethane, polyethylene, and polypropylene, are used to make various medical devices and as packaging for food. Sterilization can be accomplished by exposing the devices or packages to gamma radiation. However, the gamma radiation can degrade or yellow the polymer, making it unsuitable or less acceptable for certain applications. Polymers such as polyethylene, polypropylene, and PVC can also degrade and yellow after heating.

According to one aspect of this invention there is provided a polymer which comprises polyvinyl chloride, polyvinylidene chloride, polycarbonate, polyurethane, polyethylene, polypropylene, polyamide, polyimide, polyether, polyester, or polyvinyl acetate containing about 0.005 to about 10 phr of a stabilizer having the general formula:

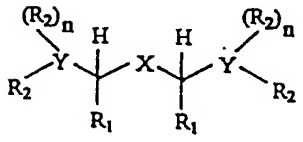
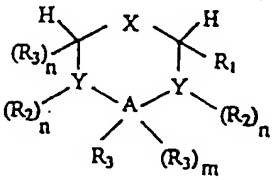
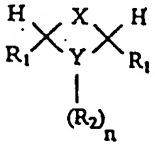
where A is C, P, Sn, Si, or B, X is =C=C=, -C≡C-,



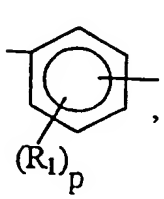
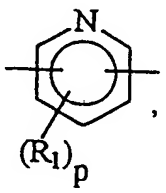
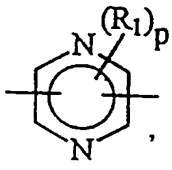
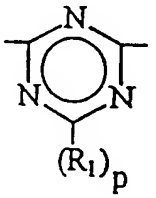
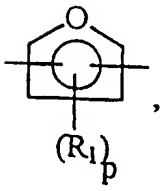
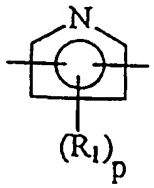
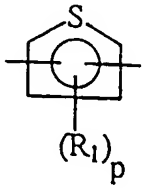
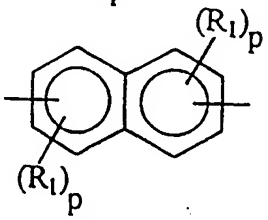
each Y is independently selected from O, S, and N, each R is independently selected from hydrogen, alkyl from C_1 to C_{24}, aryl from C_6 to C_{24}, alkaryl from C_7 to C_{24}, and aralkyl from C_7 to C_{24}. each R_1 is independently selected from R, OR, RCO, ROCO, $ROCO_2$, $P(R)_2$, $P(OR)_2$, $PR(OR)$, $N(R)_2$, $(R)_2NCO$, $(R)_2NCO_2$, SR, and halogen, where two R_1 groups can be bridged together to form a ring, each R_2 is independently selected from R, RCO, ROCO, $P(OR)_2$, $Sn(R)_q(OR)_{3-q}$, $SnR_q(OCOR)_{3-q}$, $Si(R)_q(OR)_{3-q}$, and $BR_q(OR)_{2-q}$, where two R_2 groups can be bridged together to form a ring, each R_3 is independently selected from R, RCO, ROCO, $ROCO_2$, OR, SR, $N(R)_2$, $OP(R)_2$, and $OP(OR)_2$, m is 0 when A is P or B and is 1 when A is Sn, Si, or C, n is 0 when Y is O or S and is 1 when Y is N, p is 0 to 4, depending on the number of available sites, and q is 0 to 3 for the tin stabilizers and 0 to 2 for the boron stabilizers.

When a particular type of stabilizer is added to certain polymers the polymers degrade and yellow substantially less after exposure to oxidation. Some of the stabilizers of this invention are novel compounds while others are commercially available. Some of these stabilizers are polymeric and resist leaching or migration from the polymer, thereby further extending the life of the polymer.

The stabilizers of this invention have the general fomula:

where A is C, P, Sn, Si, or B, X is =C=C=, -C≡C-,

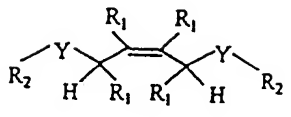









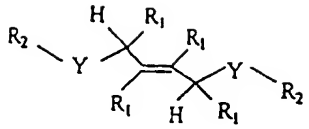
each Y is independently selected from O, S, and N, each R is independently selected from hydrogen, alkyl from C_1 to C_{24}, aryl from C_6 to C_{24}, alkaryl from C_7 to C_{24}, and aralkyl from C_7 to C_{24}, each R_1 is independently selected from R, OR, RCO, ROCO, $ROCO_2$, $P(R)_2$, $P(OR)_2$, PR(OR), $N(R)_2$, $(R)_2NCO$, $(R)_2NCO_2$, SR, and halogen, where two R_1 groups can be bridged together to form a ring, each R_2 is independently

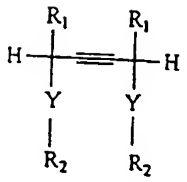
selected from R, RCO, ROCO, $P(OR)_2$, $Sn(R)_q(OR)_{3-q}$, $SnR_q(OCOR)_{3-q}$, $Si(R)_q(OR)_{3-q}$, and $BR_q(OR)_{2-q}$, where two R_2 groups can be bridged together to form a ring, each R_3 is independently selected from R, RCO, ROCO, $ROCO_2$, OR, SR, $N(R)_2$, $OP(R)_2$, and $OP(OR)_2$, m is 0 when A is P or B and is 1 when A is Sn, Si, or C, n is 0 when Y is O or S and is 1 when Y is N, p is 0 to 4, depending on the number of available sites, and q is 0 to 3 for the tin stabilizers and 0 to 2 for the boron stabilizers. Groups that can bridge two R_1 or two R_2 groups together to form a ring include R_4, -HC=CH-, $-CH_2O-$, $-CH_2NH-$, -HC=N-, and $-CH_2S$, where R_4 is alkylene from C_1 to C_{24}, arylene from C_6 to C_{24}, (aryl)alkylene from C_7 to C_{24}, (alkyl)arylene from C_7 to C_{24}, alkanediyl from C_1 to C_{24}, (aryl)alkanediyl from C_7 to C_{24}, -CO-(alkylene)-CO- from C_1 to C_{24}, -CO-arylene-CO- from C_6 to C_{24}, -CO-(aryl)alkylene-CO- from C_7 to C_{24}, -CO-(alkyl)arylene-CO)- from C_7 to C_{24}, $Si(R)_2$, SiR(OR), $Si(OR)_2$, P(OR), B(OR), $Sn(R)_2$, SnR(OR), or SnR(O-CO-R).

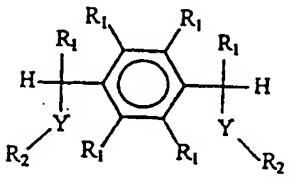
Preferably, A is C, X is -HC=HC-, Y is O, R is benzyl, R_1 is H, R_2 is R_1, R_3 is R_1 R_4 is alkylene from C_1 to C_8, (aryl)alkylene from C_7 to C_8, or -CO-(aryl)alkylene-CO- from C_7 to C_8, and q is O because those compounds work well and are readily available. Stabilizers where each R_1 is hydrogen are especially preferred as they are more effective. When X is =C=C= the stabilizers can be either cis or trans, but the cis stabilizers are preferred because they are less expensive.

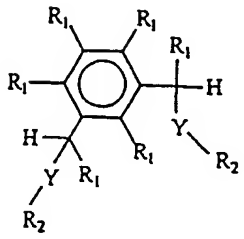
The following are examples of some of the stabilizers included within the scope of the above formulas (if Y is N, there is an additional R_3 group on Y):

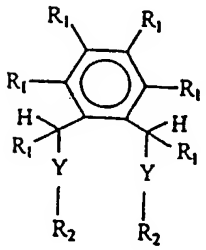


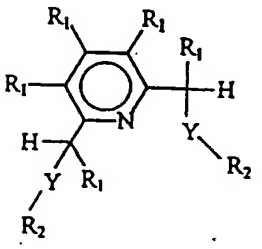


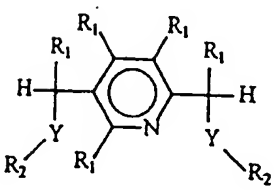


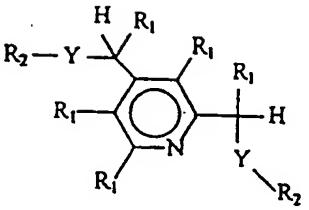


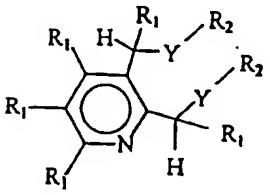


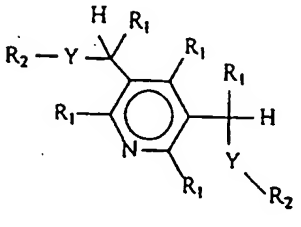


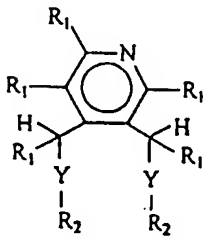


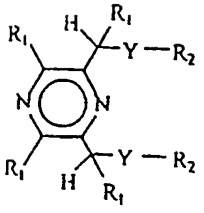
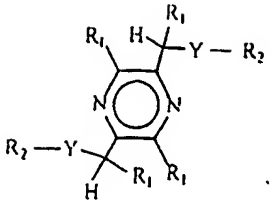
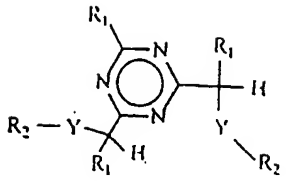
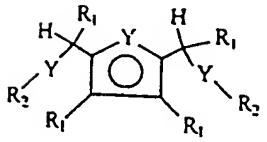
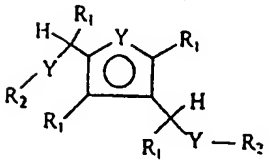
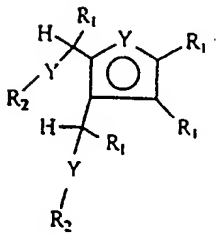
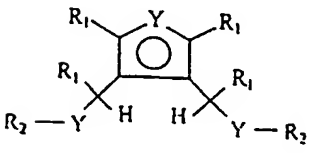
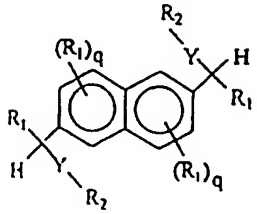










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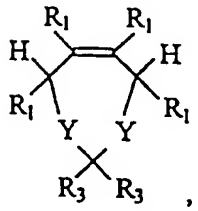
Examples of stabilizers having a cyclic structure include: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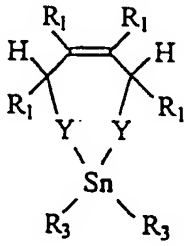
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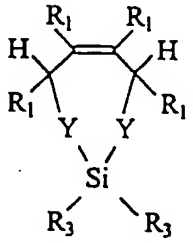
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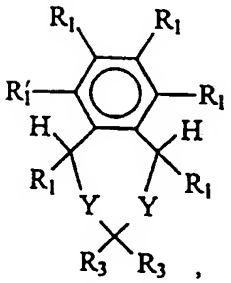
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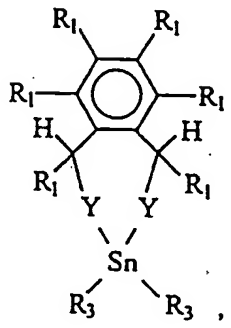
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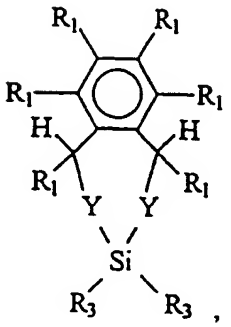
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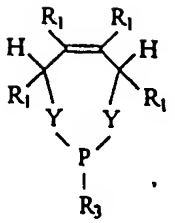
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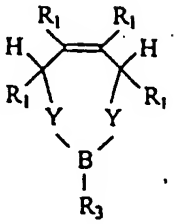
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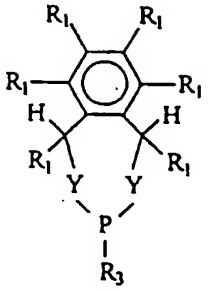
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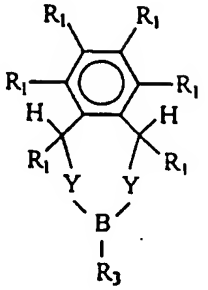
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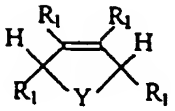
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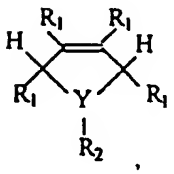
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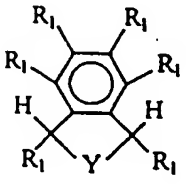
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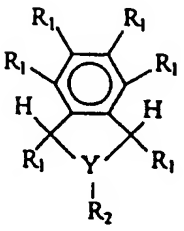
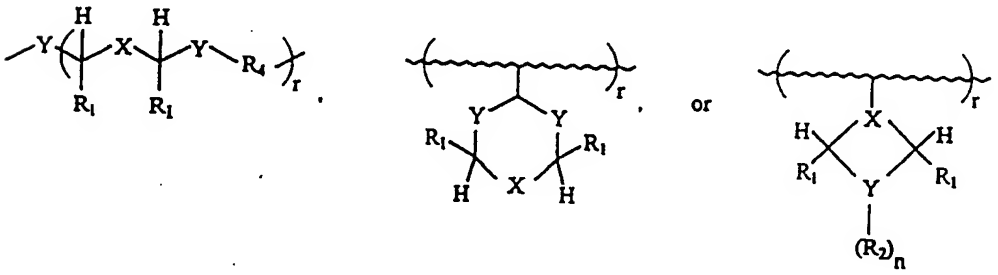


Examples of stabilizers having the above structure include 4,7-dihydro-1,3-dioxepins, ethers and esters of butene-1,4-diol, and phthalans. These stabilizers can be prepared by condensing an allylic diol, or an aromatic analog of an allylic diol, with an aldehyde, ketone, acid, acid halide, ester, alkyl halide, or alcohol or by other reactions known to those skilled in the art, to form derivatives. Preferred stabilizers include cis-2-butene-1,4-diol, cis-4-benzyloxy-2-buten-1-ol, and cis-1,4-dibenzyloxy-2-butene. The stabilizer may be a phthalan.



A B C

In the above formulas, r can be 1 to 1000, but is preferably 1 to 5. Examples of polymers having formula A include poly(2-butenylene adipate), poly(2-butenylene-terephthalate, and poly[oxy(2-butenylene)]. In formulas B and C, the preferred backbones are polyesters, polyethers, and polyketones, and the preferred pendant groups are 4,7-dihydro-1,3-dioxepin, phthalan, and 2-butene-1,4-diol. Examples of such compounds include the condensate of poly(ethylene-co-carbon monoxide) with 2-butene-1,4-diol. The polymeric stabilizers are expected to be more effective as they have less tendency to migrate or leach out of the stabilized polymer. Preparation of these polymers can be achieved by reactions known to those skilled

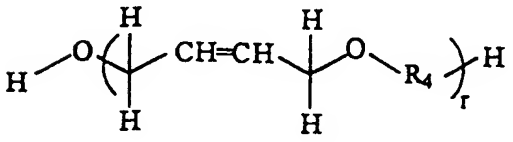
in the art. For example, the polymeric esters can be prepared by reacting the diol (see the first formulas where Y is oxygen and R_1 is hydrogen) with a diester, diacid, diacid chloride, or dianhydride.

The stabilizers of this invention are effective against oxidation of PVC, polycarbonates, polyurethane, polypropylene, polyethylene, polyvinylidene chloride, polyamides, polyimides, polyethers, polyesters, polysiloxanes, polyurethanes, polysulfones, and polysulfides. The preferred polymers are PVC, polycarbonates, polypropylene, and polyethylene because those polymers are more frequently used in medical applications where they are subjected to gamma radiation; particularly preferred is PVC. Thus the invention also relates to a polymer that has been subjected to oxidizing heat or radiation.

The polymer can be stabilized by the addition of about 0.005 to about 10 phr (parts by weight per 100 parts by weight of the polymer) of the stabilizer to the polymer. Less stabilizer is less effective and more stabilizer offers little additional benefit. The preferred amount of stabilizer is about 0.2 to about 6 phr. The stabilizer can be added to a polymer in a variety of ways, such as mixing the reactants at the beginning or during polymerization. The stabilizer is preferably added after at least 70 wt% of the monomer has polymerized. The stabilizer can be added as a solid or with a solvent as a slurry or a solution. Common organic solvents such as N-methylpyrrolidone, diglyme, acetamide, acetone, methanol, ethanol, isopropanol, dimethysulfoxide, and dimethylformamide can be used; water can also be used. Water miscible solvents, such as acetone, tetrahydrofuran, and methanol, are preferred for PVC. It is preferable to add the stabilizer in a solvent as that achieves a more uniform distribution of the stabilizer in the polymer. The stabilizer can also be added during the drying or compounding of the polymer. Various methods can

be used for compounding, including milling, dry mixing, and extrusion. The stabilizers function as antioxidants to inhibit various forms of oxidation.

The invention also provides polyvinyl chloride, polyurethane, polyethylene, polypropylene, or polycarbonate containing about 0.2 to about 6 phr of a stabilizer having the general formula:



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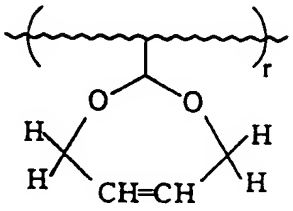

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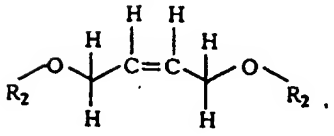

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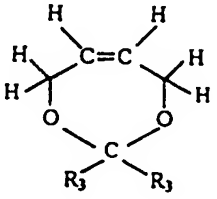

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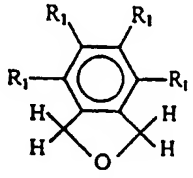
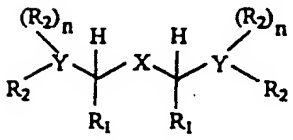


where R_2 is R, R_3 is R, R_4 is alkylene from C_1 to C_8, (aryl)alkylene from C_7 to C_8, or -CO-(aryl)alkylene-CO- from C_7 to C_8 , R is benzyl, and r is 1 to 5.

This polymer may have been subjected to gamma radiation.

The invention additionally provides a method of preventing a polymer which comprises polyvinyl chloride, polyvinylidene chloride, polycarbonate, polyethylene, polypropylene, polyamide, polyimide, polyether, polyester, or polyvinyl acetate from discoloring after exposure to oxiddation comprising mixing into said polymer about 0.005 to about 10 phr of a stabilizer having the general formula: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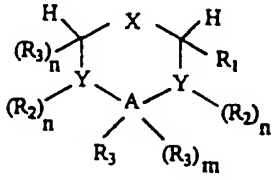
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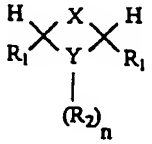
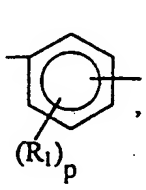


where A is C, P, Sn, Si, or B, X is =C=C=, -C≡C-,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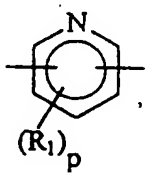
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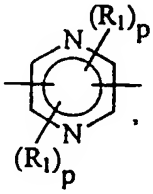
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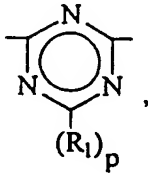
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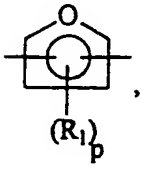
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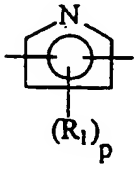
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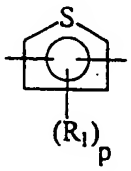
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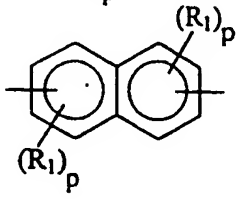


each Y is independently selected from O, S, and N, each R is independently selected from hydrogen, alkyl from C_1 to C_{24}, aryl from C_6 to C_{24}, alkaryl from C_7 to C_{24}, and

aralkyl from C_7 to C_{24}, each R_1 is independently selected from R, OR, RCO, ROCO, $ROCO_2$, $P(R)_2$, $P(OR)_2$, $PR(OR)$, $N(R)_2$, $(R)_2NCO$, $(R)_2NCO_2$, SR, and halogen, where two R_1 groups can be bridged together to form a ring, each R_2 is independently selected from R, RCO, ROCO, $P(OR)_2$, $Sn(R)_q(OR)_{3-q}$, $SnR_q(OCOR)_{3-q}$, $Si(R)_q(OR)_{3-q}$, and $BR_q(OR)_{2-q}$, where two R_2 groups can be bridged together to form a ring, each R_3 is independently selected from R, RCO, ROCO, $ROCO_2$, OR, SR, $N(R)_2$, $OP(R)_2$, and $OP(OR)_2$, m is 0 when A is P or B and is 1 when A is Sn, Si, or C, n is 0 when Y is O or S and is 1 when Y is N, p is 0 to 4, depending on the number of available sites, and q is 0 to 3 for the tin stabilizers and 0 to 2 for the boron stabilizers.

The following examples further illustrate this invention.

EXAMPLES 1 to 13

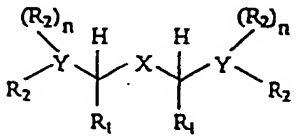
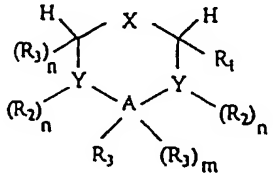
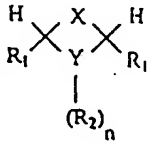
To a mixture of 150.00 g PVC (sold by Occidental Chemical Corporation as "Oxy 240"), 0.30 g stearic acid (used as a lubricant), 0.23 g of a zinc and calcium mixed salts of mixed fatty acids (used as a heat stabilizer, sold by Witco as "Mark 152 S"), 97.50g dioctyl phthalate (used as a heat stabilizer and to increase flexibility). 15.00 g epoxidized soy bean oil (used as an HCl scavenger to reduce degradation; sold by Witco as "Drapex 6.8"), was added a stabilizer. The mixture was thoroughly blended and hot milled at 149°C (300°F) for 5 minutes. The resulting PVC sheet was cut and pressed into a 4"x3"x1/4" (10x8x0.6 cm) plaque at 165.5°C (330°F). The plaque was divided into two smaller pieces. One was saved for comparison and one was subjected to γ radiation at a dose of 50 kGy. The irradiated piece was again divided into two pieces and one of these pieces was oven aged at 50°C for 48 hours. All of the samples were measured for yellowness index with a Macbeth 2020 Plus Color Eye Spectrometer, as described by the Hunter equations (see "The Measurement of Appearance" by Richard S. Hunter, John Wiley & Sons, New York, 1975). The following table gives the stabilizers used and the results.

Example	Stabilizer	Amount (g)	Yellowness		
			Initial	After Radiation	After Aging
1	2,5-dimethoxy-2,5-dihydrofuran	0.64	17.1	47.8	69.3
Control	none		18.4	52.8	74.1
2	phthalan	1.34	17.5	31.9	49.5
Control	none		18.1	50.2	75.5
3	2-butene-1.4-diol	0.75	15.7	29.7	49.4
Control	none		16.3	43.3	66.6
4	2-butene-1,4-diol	3.20	17.1	22.2	33.1
Control	none		16.3	43.3	66.6
5	cis-4-benzyloxy-2-buten-1-ol	1.67	16.6	21.1	30.7
Control	none		16.3	43.3	66.6
6	1,4-dibenzyloxy-2-butene	2.23	17.6	23.9	38.2
Control	none		16.3	43.3	66.6
7	trans-2,3-dibromo-2-butene-1,4-diol	2.06	31.8	37.6	61.7
Control	none		16.3	43.3	66.6
8	4,7-dihydro-2-phenyl-1,3-dioxepin	1.47	16.1	26.0	41.1
Control	none		16.3	43.3	66.6
9	2,2'-(1,4-phenylene)bis(4,7-dihydro-1,3-dioxepin)	2.40	24.3	36.5	40.9
Control	none		18.1	50.2	75.5
10	1,5-dihydro-3-methoxy-2,4-benzodioxepin	2.03	16.7	36.0	49.8
Control	none		18.1	50.2	75.5
11	2-butyne-1,4-diol	0.96	18.0	39.9	62.9
Control	none		18.1	50.2	75.5
12	1,4-bis(2-hydroxyethoxy)-2-butyne	1.99	32.0	31.6	40.2
Control	none		18.1	50.2	75.5
13	1,4-benzenedimethanol	1.50	21.0	41.1	47.7
Control	none		18.1	50.2	75.5

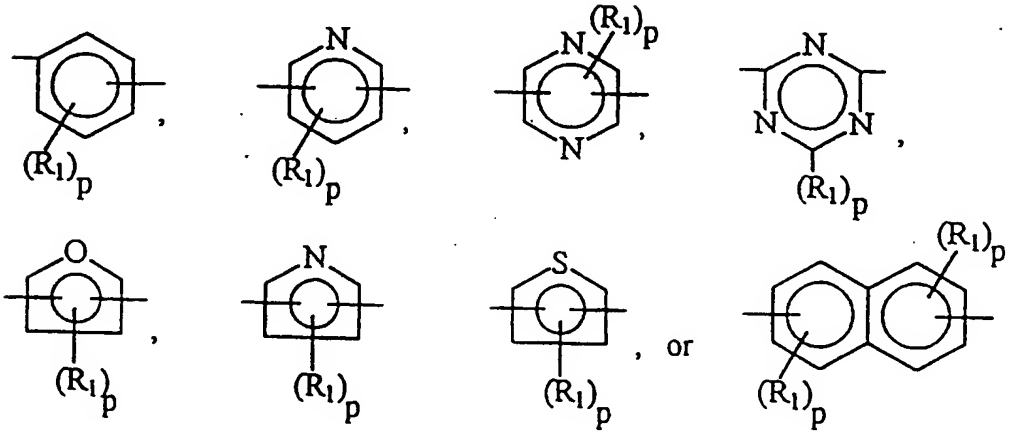
As can be observed from the above table, after γ radiation the polymers that contained a stabilizer had significantly less discoloration than the control samples.

CLAIMS:

1. A polymer which comprises polyvinyl chloride, polyvinylidene chloride, polycarbonate, polyurethane, polyethylene, polypropylene, polyamide, polyimide, polyether, polyester, or polyvinyl acetate containing about 0.005 to about 10 phr of a stabilizer having the general formula:

where A is C, P, Sn, Si; or B, X is =C=C=, -C≡C-,

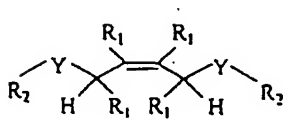
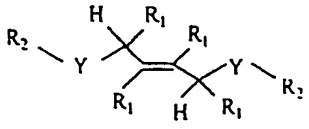
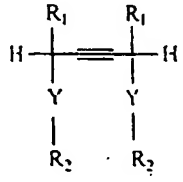
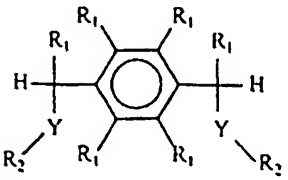
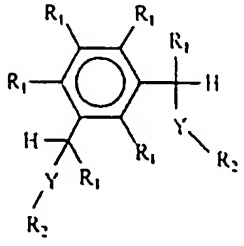
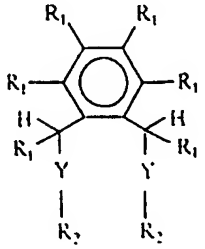


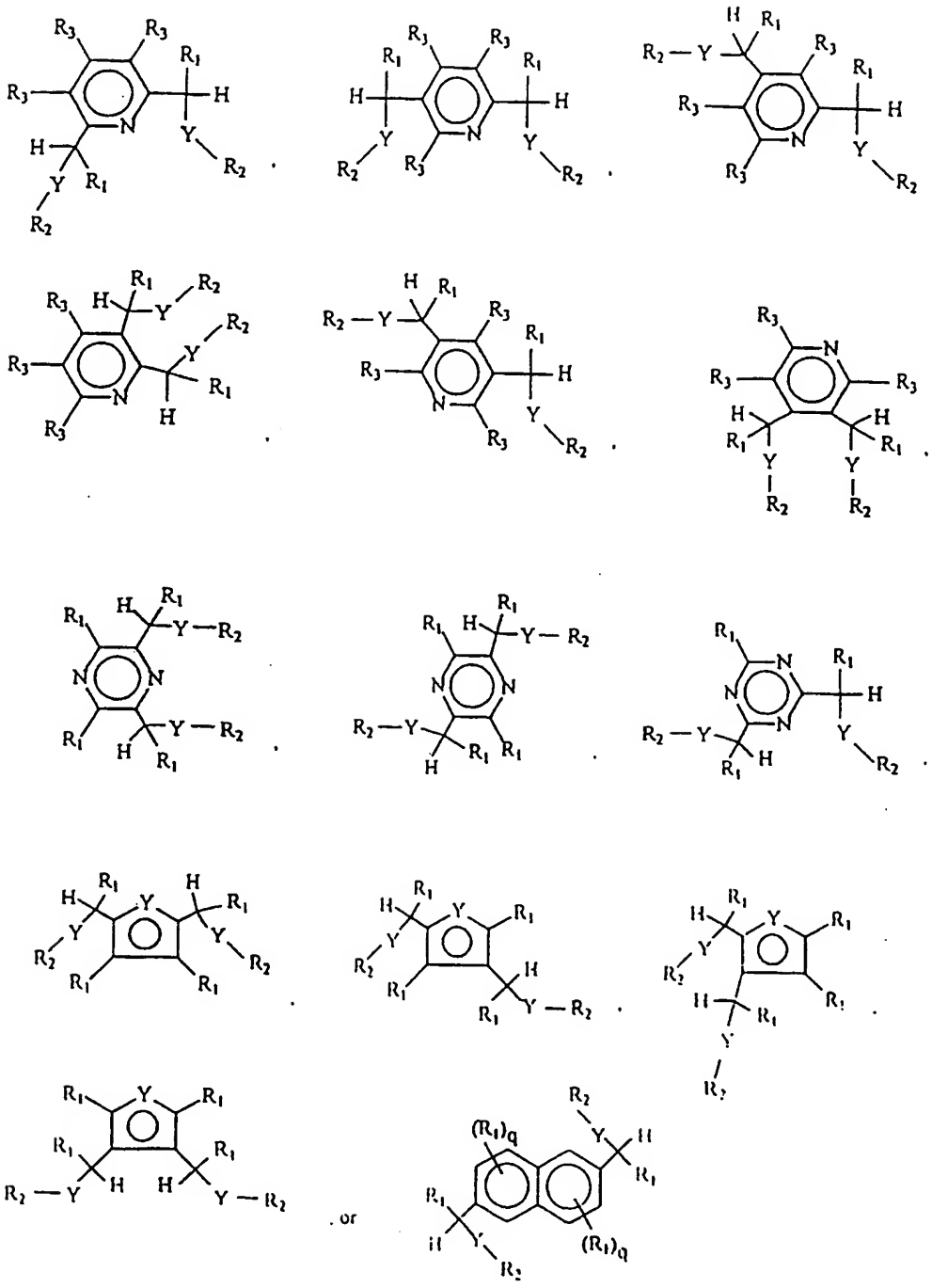
each Y is independently selected from O, S, and N, each R is independently selected from hydrogen, alkyl from C_1 to C_{24}, aryl from C_6 to C_{24}, alkaryl from C_7 to C_{24}, and aralkyl from C_7 to C_{24}, each R_1 is independently selected from R, OR, RCO, ROCO, $ROCO_2$, $P(R)_2$, $P(OR)_2$, $PR(OR)$, $N(R)_2$, $(R)_2NCO$, $(R)_2NCO_2$, SR, and halogen, where

two R_1 groups can be bridged together to form a ring, each R_2 is independently selected from R, RCO, ROCO, $P(OR)_2$, $Sn(R)_q(OR)_{3-q}$, $SnR_q(OCOR)_{3-q}$, $Si(R)_q(OR)_{3-q}$, and $BR_q(OR)_{2-q}$, where two R_2 groups can be bridged together to form a ring, each R_3 is independently selected from R, RCO, ROCO, $ROCO_2$, OR, SR, $N(R)_2$, $OP(R)_2$, and $OP(OR)_2$, m is 0 when A is P or B and is 1 when A is Sn, Si, or C, n is 0 when Y is O or S and is 1 when Y is N, p is 0 to 4, depending on the number of available sites, and q is 0 to 3 for the tin stabilizers and 0 to 2 for the boron stabilizers.

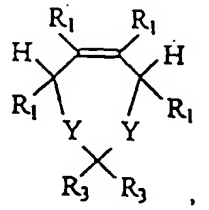
2. A polymer according to Claim 1 wherein said polymer is polyvinyl chloride.

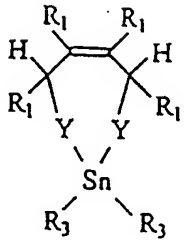
3. A polymer according to Claim 1 wherein said stabilizer has the general formula

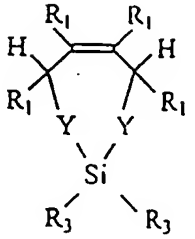







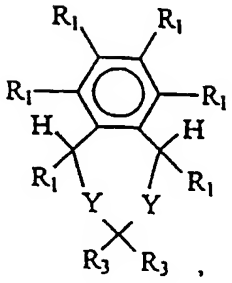


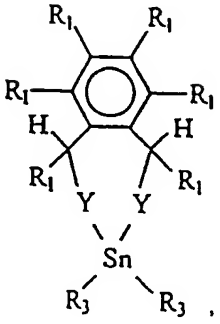
4. A polymer according to Claim 1 wherein said stabilizer has the general formula:

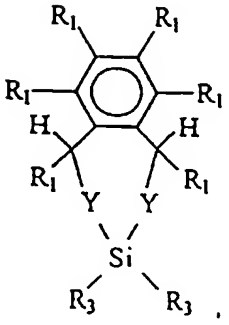


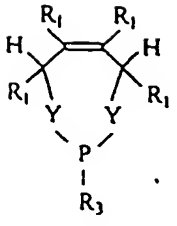


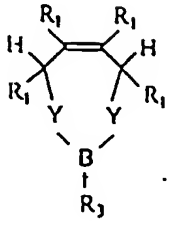


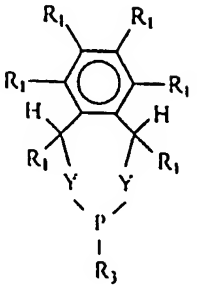


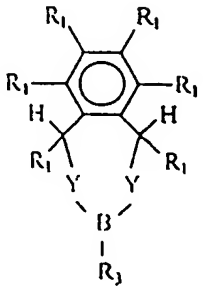


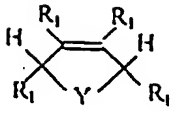


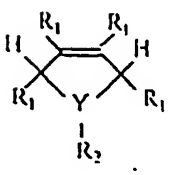


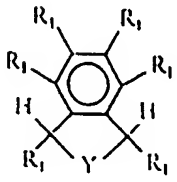




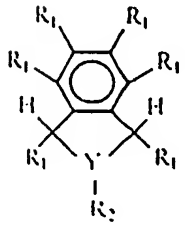








or



5. A polymer according to Claim 1 wherein said stabilizer is cis-2-butene-1,4-diol.

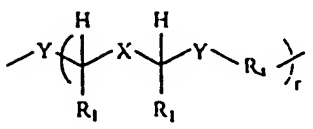
6. A polymer according to Claim 1 wherein said stabilizer is cis-4-benzyloxy-2-buten-1-ol.

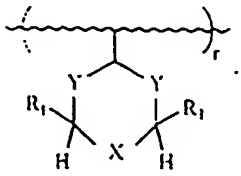
7. A polymer according to Claim 1 wherein said stabilizer is cis-1,4-dibenzyloxy-2-butene.

8. A polymer according to Claim 1 wherein said stabilizer is a 4,7-dihydro-1,3-dioxepin.

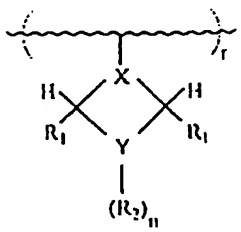
9. A polymer according to Claim 1 wherein said stabilizer is a phthalan.

10. A polymer according to Claim 1 wherein said stabilizer has the structure:





or



where R_4 is alkylene from C_1 to C_{24}, arylene from C_6 to C_{24}, (aryl)alkylene from C_7 to C_{24}, (alkyl)arylene from C_7 to C_{24}, alkanediyl from C_1 to C_{24}, (aryl)alkanediyl from C_7 to C_{24}, -CO-(alkylene)-CO- from C_1 to C_{24}, -CO-arylene-CO- from C_6 to C_{24}, -CO-(aryl)alkylene-CO- from C_7 to C_{24}, -CO-(alkyl)arylene-CO)- from C_7 to C_{24}, $Si(R)_2$, SiR(OR), $Si(OR)_2$, P(OR), B(OR), $Sn(R)_2$, SnR(OR), or SnR(O-CO-R), and r is 1 to 1000.

11. A polymer according to Claim 10 wherein said stabilizer has pendant 4,7-dihydro-1,3-dioxepin groups.

12. A polymer according to Claim 10 wherein said stabilizer has pendant phthalan groups.

13. A polymer according to Claim 10 wherein said stabilizer has pendant 2-butene-1,4-diol groups.

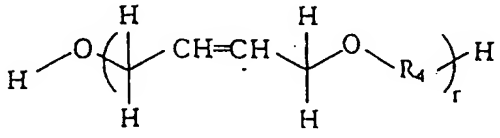
14. A polymer according to Claim 10 wherein said stabilizer is a polyether having pendant 2-butene-1,4-diol groups.

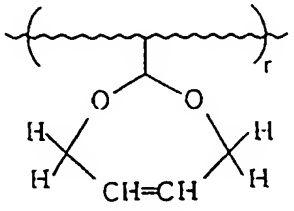
15. A polymer according to Claim 10 wherein said stabilizer is a polyester having pendant 2-butene-1,4-diol groups.

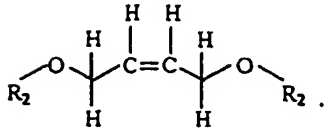
16. A polymer according to Claim 1 wherein A is C, X is -HC=CH-, Y is O, R is benzyl, R_1 is H, R_2 is R, R_3 is R, R_4 is alkylene from C_1 to C_8, (aryl)alkylene from C_6 to C_8, or -CO-(aryl)alkylene-CO- from C_6 to C_8, or q is 0.

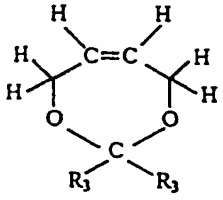
17. A polymer according to any one of the preceding Claims that has been subjected to oxidizing heat or radiation.

18. Polyvinyl chloride, polyurethane, polyethylene, polypropylene, or polycarbonate containing about 0.2 to about 6 phr of a stabilizer having the general formula:

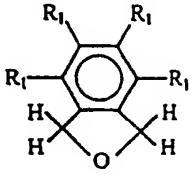








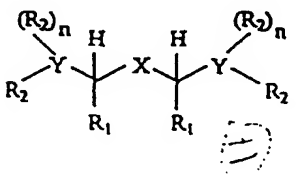
. or

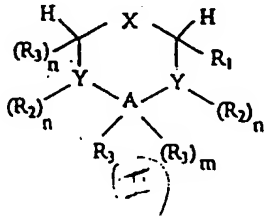


where R_2 is R, R_3 is R, R_4 is alkylene from C_1 to C_8, (aryl)alkylene from C_7 to C_8, or -CO-(aryl)alkylene-CO- from C_7 to C_8, R is benzyl, and r is 1 to 5.

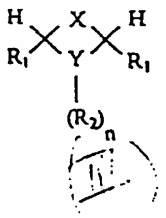
19. Polyvinyl chloride according to Claim 18 that has been subjected to gamma radiation..

20. A method of preventing a polymer which comprises polyvinyl chloride, polyvinylidene chloride, polycarbonate, polyethylene, polypropylene, polyamide, polyimide, polyether, polyester, or polyvinyl acetate from discoloring after exposure to oxidation comprising mixing into said polymer about 0.005 to about 10 phr of a stabilizer having the general formula:

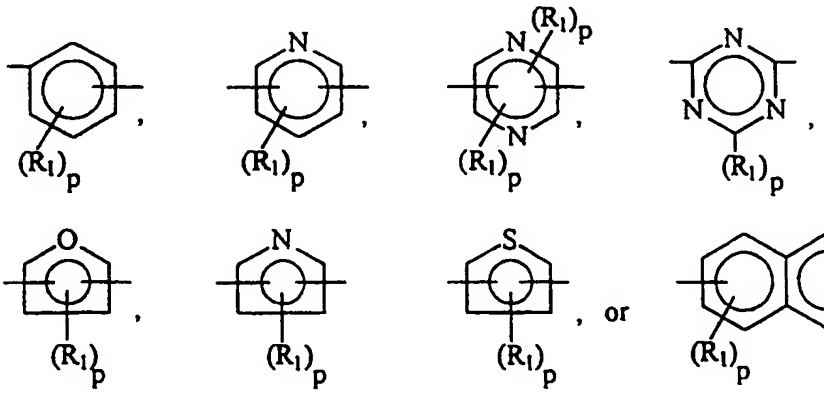




. or



where A is C, P, Sn, Si, or B, X is =C=C=, -C≡C-,



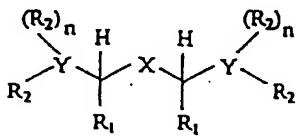
each Y is independently selected from O, S, and N, each R is independently selected from hydrogen, alkyl from C_1 to C_{24}, aryl from C_6 to C_{24}, alkaryl from C_7 to C_{24}, and

aralkyl from C_7 to C_{24}, each R_1 is independently selected from R, OR, RCO, ROCO, $ROCO_2$, $P(R)_2$, $P(OR)_2$, PR(OR), $N(R)_2$, $(R)_2NCO$, $(R)_2NCO_2$, SR, and halogen, where two R_1 groups can be bridged together to form a ring, each R_2 is independently selected from R, RCO, ROCO, $P(OR)_2$, $Sn(R)_q(OR)_{3-q}$, $SnR_q(OCOR)_{3-q}$, $Si(R)_q(OR)_{3-q}$, and $BR_q(OR)_{2-q}$, where two R_2 groups can be bridged together to form a ring, each R_3 is independently selected from R, RCO, ROCO, $ROCO_2$, OR, SR, $N(R)_2$, $OP(R)_2$, and $OP(OR)_2$, m is 0 when A is P or B and is 1 when A is Sn, Si, or C, n is 0 when Y is O or S and is 1 when Y is N, p is 0 to 4, depending on the number of available sites, and q is 0 to 3 for the tin stabilizers and 0 to 2 for the boron stabilizers.

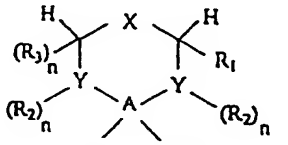
AMENDED CLAIMS

[received by the International Bureau on 18 July 2000 (18.07.00); original claims 1, 5-20 replaced by new claims 1, 5-16; remaining claims unchanged (8 pages)]

1. A polymer which comprises polyvinyl chloride, polyvinylidene chloride, polycarbonate, polyurethane, polyethylene, polypropylene, polyamide, polyimide, polyether, polyester, or polyvinyl acetate containing about 0.005 to about 10 phr of a stabilizer having the general formula:

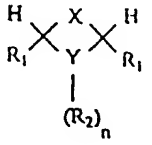


(I)

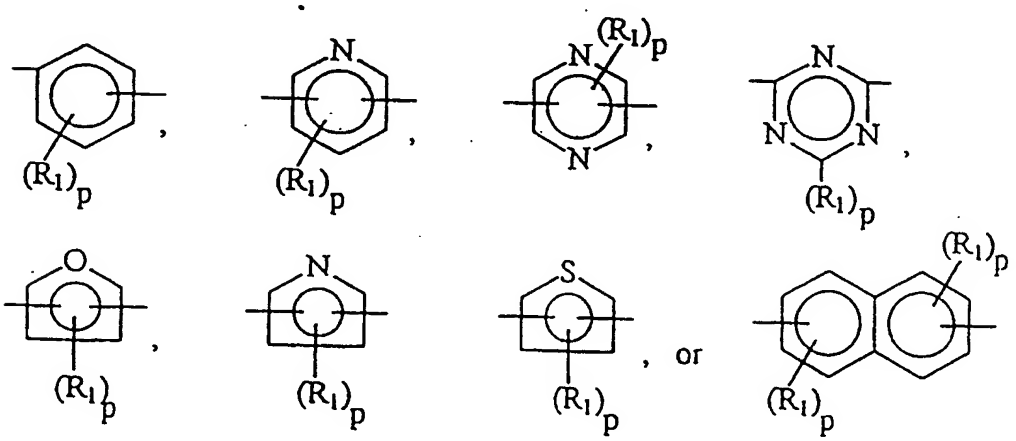


(II)

. or



where A is C, P, Sn, Si; or B, X is $-R_1C=CR_1-$, $-C\equiv C-$,



each Y is independently selected from O, S, and N, each R is independently selected from hydrogen, alkyl from C_1 to C_{24}, aryl from C_6 to C_{24}, alkaryl from C_7 to C_{24}, and aralkyl from C_7 to C_{24}, each R_1 is independently selected from R, OR, RCO, ROCO, $ROCO_2$, $P(R)_2$, $P(OR)_2$, PR(OR), $N(R)_2$, $(R)_2NCO$, $(R)_2NCO_2$, SR, and halogen, where

two R_1 groups can be bridged together to form a ring, each R_2 is independently selected from R, RCO, ROCO, $P(OR)_2$, $Sn(R)_q(OR)_{3-q}$, $SnR_q(OCOR)_{3-q}$, $Si(R)_q(OR)_{3-q}$, and $BR_q(OR)_{2-q}$, where two R_2 groups can be bridged together to form a ring, each R_3 is independently selected from R, RCO, ROCO, $ROCO_2$, OR, SR, $N(R)_2$, $OP(R)_2$, and $OP(OR)_2$, m is 0 when A is P or B and is 1 when A is Sn, Si, or C, n is 0 when Y is O or S and is 1 when Y is N, p is 0 to 4, depending on the number of available sites, and q is 0 to 3 for the tin stabilizers and 0 to 2 for the boron stabilizers,

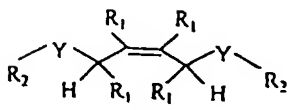
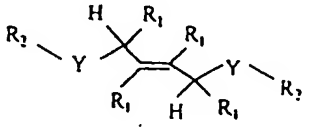
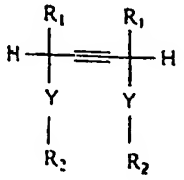
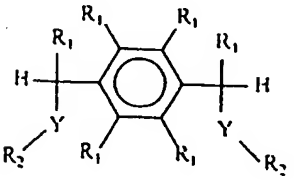
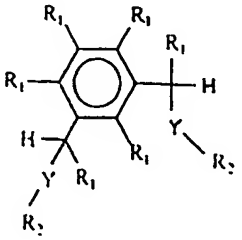
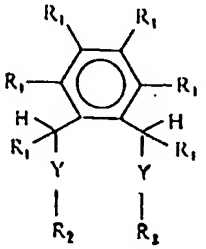
with the provisos that;

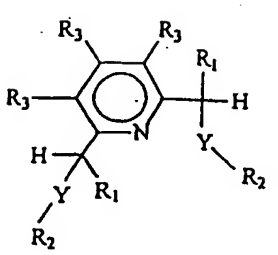
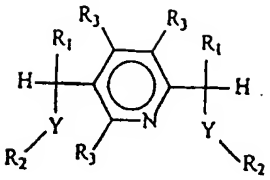
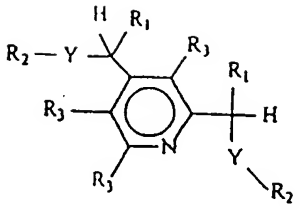
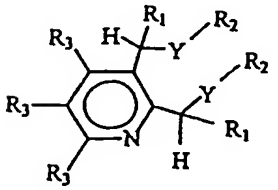
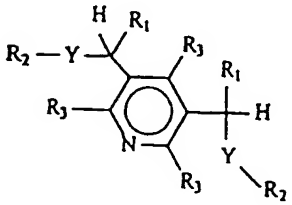
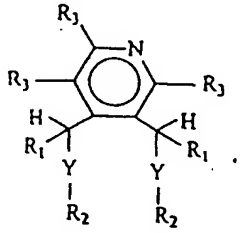
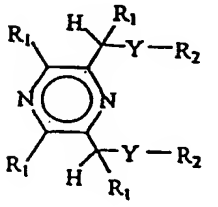
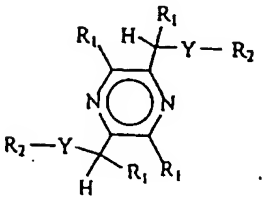
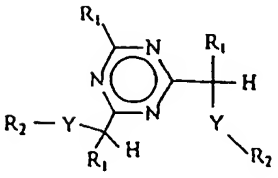
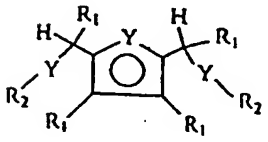
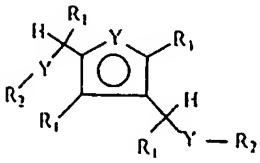
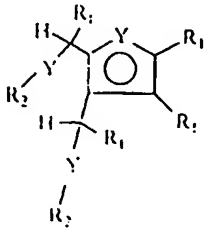
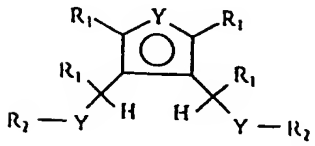
in general formula (I), when X= -HC=CH-, Y=O and R_2=H, then at least one of the R_1 groups is not H; and,

in general formula (II), when X= $-R_1C=CR_1-$, Y=O and A=C, then at least one of the R_3 groups on A is not hydrogen.

2. A polymer according to Claim 1 wherein said polymer is polyvinyl chloride.

3. A polymer according to Claim 1 wherein said stabilizer has the general formula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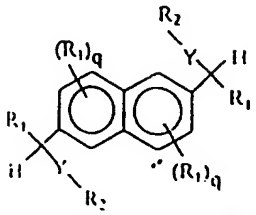
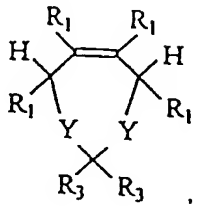
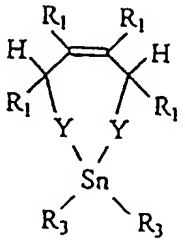
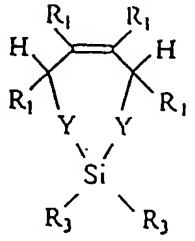
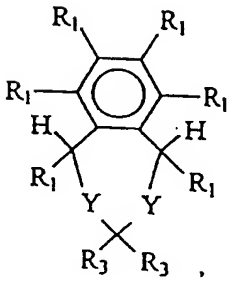
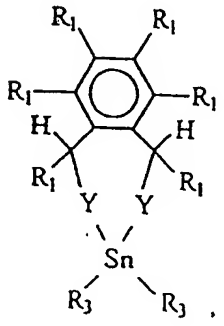
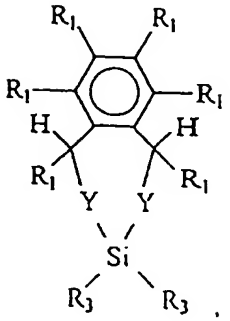
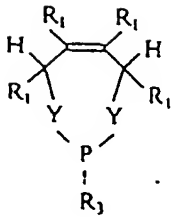
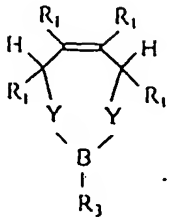
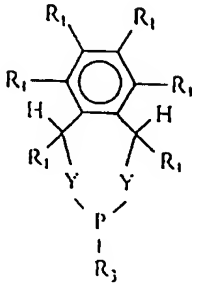
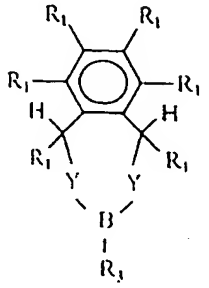
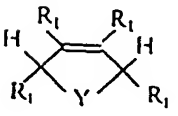
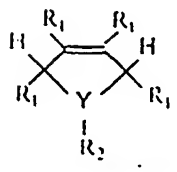
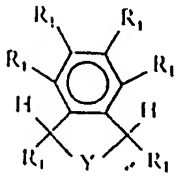


4. A polymer according to Claim 1 wherein said stabilizer has the general formula: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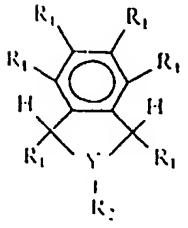


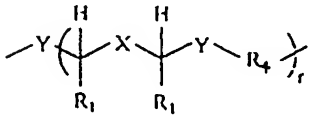
5. A polymer according to Claim 1 wherein said stabilizer is cis-4-benzyloxy-2-buten-1-ol.

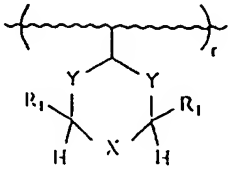
6. A polymer according to Claim 1 wherein said stabilizer is cis-1,4-dibenzyloxy-2-butene.

7. A polymer according to Claim 1 wherein said stabilizer is a 4,7-dihydro-1,3-dioxepin.

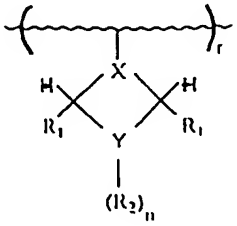
8. A polymer according to Claim 1 wherein said stabilizer is a phthalan.

9. A polymer according to Claim 1 wherein said stabilizer has the structure:





or



where R_4 is alkylene from C_1 to C_{24}, arylene from C_6 to C_{24}, (aryl)alkylene from C_7 to C_{24}, (alkyl)arylene from C_7 to C_{24}, alkanediyl from C_1 to C_{24}, (aryl)alkanediyl from C_7 to C_{24}, -CO-(alkylene)-CO- from C_1 to C_{24}, -CO-arylene-CO- from C_6 to C_{24}, -CO-(aryl)alkylene-CO- from C_7 to C_{24}, -CO-(alkyl)arylene-CO)- from C_7 to C_{24}, $Si(R)_2$, SiR(OR), $Si(OR)_2$, P(OR), B(OR), $Sn(R)_2$, SnR(OR), or SnR(O-CO-R), and r is 1 to 1000.

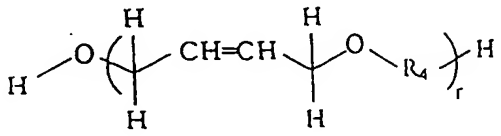
10. **A polymer according to Claim 9 wherein said stabilizer has pendant 4,7-dihydro-1,3-dioxepin groups.**

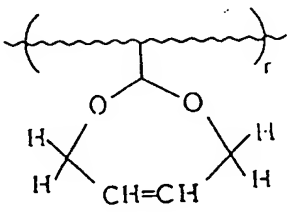
11. **A polymer according to Claim 9 wherein said stabilizer has pendant phthalan groups.**

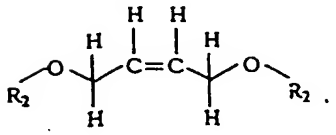
12. A polymer according to Claim 1 wherein A is C, X is -HC=CH-, Y is O, R is benzyl, R_1 is H, R_2 is R, R_3 is R, R_4 is alkylene from C_1 to C_8, (aryl)alkylene from C_6 to C_8, or -CO-(aryl)alkylene-CO- from C_6 to C_8, or q is 0.

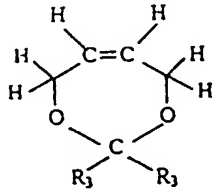
13. A polymer according to any one of the preceding Claims that has been subjected to oxidizing heat or radiation.

14. Polyvinyl chloride, polyurethane, polyethylene, polypropylene, or polycarbonate containing about 0.2 to about 6 phr of a stabilizer having the general formula:

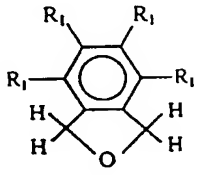








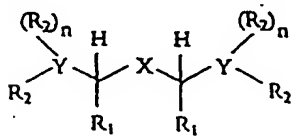
. or

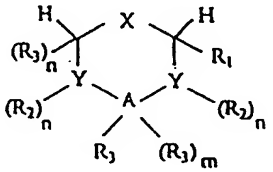


where R_2 is R, R_3 is R, R_4 is alkylene from C_1 to C_6, (aryl)alkylene from C_7 to C_8, or -CO-(aryl)alkylene-CO- from C_7 to C_8, R is benzyl, and r is 1 to 5.

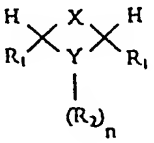
15. Polyvinyl chloride according to Claim 14 that has been subjected to gamma radiation.

16. A method of preventing a polymer which comprises polyvinyl chloride, polyvinylidene chloride, polycarbonate, polyethylene, polypropylene, polyamide, polyimide, polyether, polyester, or polyvinyl acetate from discoloring after exposure to oxidation comprising mixing into said polymer about 0.005 to about 10 phr of a stabilizer having the general formula:

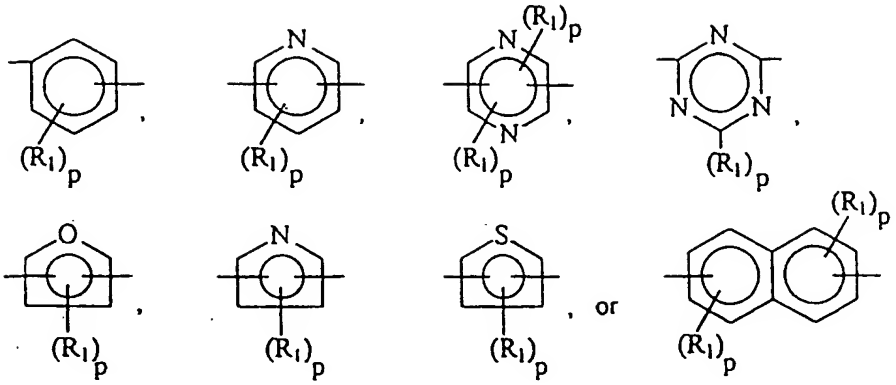




. or



where A is C, P, Sn, Si, or B, X is $-R_1C=CR_1-$, $-C\equiv C-$,



each Y is independently selected from O, S, and N, each R is independently selected from hydrogen, alkyl from C_1 to C_{24}, aryl from C_6 to C_{24}, alkaryl from C_7 to C_{24}, and aralkyl from C_7 to C_{24}, each R_1 is independently selected from R, OR, RCO, ROCO, $ROCO_2$, $P(R)_2$, $P(OR)_2$, $PR(OR)$, $N(R)_2$, $(R)_2NCO$, $(R)_2NCO_2$, SR, and halogen, where two R_1 groups can be bridged together to form a ring, each R_2 is independently selected from R, RCO, ROCO, $P(OR)_2$, $Sn(R)_q(OR)_{3-q}$, $SnR_q(OCOR)_{3-q}$, $Si(R)_q(OR)_{3-q}$, and $BR_q(OR)_{2-q}$, where two R_2 groups can be bridged together to form a ring, each R_3 is independently selected from R, RCO, ROCO, $ROCO_2$, OR, SR, $N(R)_2$, $OP(R)_2$, and $OP(OR)_2$, m is 0 when A is P or B and is 1 when A is Sn, Si, or C, n is 0 when Y is O or S and is 1 when Y is N, p is 0 to 4, depending on the number of available sites, and q is 0 to 3 for the tin stabilizers and 0 to 2 for the boron stabilizers,

with the provisos that;

in general formula (I), when X= -HC=CH-, Y=O and R_2=H, then at least one of the R_1 groups is not H; and,

in general formula (II), when X= $-R_1C=CR_1-$, Y=O and A=C, then at least one of the R_3 groups on A is not hydrogen.

INTERNATIONAL SEARCH REPORT

Internat I Application No
PCT/GB 00/00247

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08K5/00 C08K5/053 C08K5/15 C08K5/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 36 21 958 A (GRACE W R & CO) 15 January 1987 (1987-01-15) page 6, line 20-24; table B ---	1,5
X	EP 0 584 679 A (MITSUBISHI PETROCHEMICAL CO) 2 March 1994 (1994-03-02) abstract page 4, line 31-33 -----	1,8

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
5 April 2000	28. 04. 2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Friederich, P

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Inten..ional application No.
PCT/GB 00/00247

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 2-4,10-20
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 2-4,10-20

Present claims 1-20 relate to an extremely large number of possible compounds. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the compounds claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the compounds of the page 14 in the description.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

information on patent family members

Inter ›nal Application No
PCT/GB 00/00247

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 3621958 A	15-01-1987	US 4686148 A	11-08-1987
		AU 5837986 A	22-01-1987
		BR 8602389 A	17-03-1987
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		JP 62036447 A	17-02-1987
		MX 164826 B	28-09-1992
		NL 8601009 A	02-02-1987
		NZ 215713 A	29-08-1989
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		DE 69303240 D	25-07-1996
		DE 69303240 T	12-12-1996
		US 5352721 A	04-10-1994